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FURTHER STUDIES ON THE ANODIZATION OF LEAD IN SULFURIC ACID SOLUTION

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ABSTRACT

The anodic corrosion of lead in sulfuric acid was studied over a wide range of potential. From existing thermodynamic data, the potentials for the occurrence of various oxidizing reactions were calculated, and experimentally it was found that most of these reactions occur at their expected potentials. In addition the solid-phase reaction $PbO_2 + Pb \rightarrow 2\ PbO$ is indicated to occur below a certain potential. The relatively large number of reactions occurring resulted in a complicated corrosion-rate vs. potential relationship.

Kinetic treatment was only partially successful. A peak in the rate-potential curve was found, below which the electrical resistance of a porous PbO-$PbSO_4$ film controls the corrosion rate. Above the potential of the peak, but below the reversible $PbO_2/PbSO_4$ potential, i.e., corresponding to discharge potentials for the positive plate, conversion of the protective PbO_2 film to $PbSO_4$ occurs and the rate is controlled by diffusion of the electrolyte into the PbO_2-$PbSO_4$ film. In other potential ranges only qualitative descriptions of the rate-controlling processes are as yet possible.

PROBLEM STATUS

This is an interim report; work is continuing.

AUTHORIZATION

NRL Problem C05-04
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FURTHER STUDIES ON THE ANODIZATION OF LEAD IN SULFURIC ACID SOLUTION

INTRODUCTION

A previous report has shown data for corrosion of lead in sulfuric acid using constant-potential techniques.[1] The potential range from about 0.1 to 1.0 volts less noble than the $PbO_2/PbSO_4$ reversible potential was studied, and a few preliminary experiments were carried out at more noble potentials. More recently, corrosion has been studied in detail at potentials about and above the positive-plate potential, because at these potentials corrosion rates are more directly related to conditions of battery service. The work was done in an attempt to elucidate the kinetics and the thermodynamics of the corrosion process in the hope that results might indicate methods of slowing down or preventing corrosion, and thus extending battery life.

In addition, with the advent of the "atomic" submarine it is expected that the battery will shift from a cycling to a stand-by type of service. Consequently, it will be necessary to know how corrosion rates vary for potentials at and above the $PbO_2/PbSO_4$ reversible potential in order to determine operating conditions which lead to maximum life under this new type of service.

THERMODYNAMIC THEORY

Considering the thermodynamics of the corrosion process, it may be stated that substantially complete knowledge of the over-all reactions possible under the various conditions of oxidation has been worked out from the available thermodynamic data.[2] Moreover, it has been found experimentally that most of the reactions expected do actually occur.

For purposes of reference, the standard electrode potentials for some reactions in the electrochemistry of lead are given in Fig. 1 and the discussion to follow will tell what reactions are to be expected in the several potential ranges involved in the corrosion study.

The electrochemical couples H_2/H^+ and Hg/Hg_2SO_4 are included for reference. The oxidation of water to oxygen is theoretically reversible at 1.23 volts; but actually it is subject to such a large overvoltage that O_2 production is not observed except at potentials several tenths of a volt more noble than the reversible potential for the $PbO_2/PbSO_4$ couple.

The potential limit of the reaction of $Pb + PbO_2 \rightarrow 2\ PbO$, which has been shown to take place in the solid phase,[3] is placed at +1.58 volts. This potential cannot be calculated from the thermodynamic data. It is believed that the occurrence of the reaction during the anodization of lead and the potential at which it is limited may be inferred from the data of this report, as will discussed later. Here, it will be assumed that the reaction does in fact occur below the potential given. Unlike the other electrochemical reactions, this potential is not a reversible one; it does not represent a point at which a net forward or reverse reaction begins to occur. It may be rationalized that, in order for the reaction to proceed, electrons must be pulled from the Pb by the PbO_2; if so, the possibility exists that the lead may be polarized to some positive voltage beyond which the PbO_2 can no longer pull away electrons, thus effectively stopping the reaction. It is to be expected that this potential will not vary with concentration of reactants and products as do the reversible potentials.

E_0	Reaction
-0.355	$Pb + H_2SO_4 \rightleftharpoons PbSO_4 + 2H^+ + 2e$
0	$H_2 \rightleftharpoons 2H^+ + 2e$
+0.252	$Pb + H_2O \rightleftharpoons PbO + 2H^+ + 2e$ $(Pb + 2\,H_2O \rightleftharpoons Pb(OH)_2 + 2H^+ + 2e)$
+0.616	$2\,Hg + H_2SO_4 \rightleftharpoons Hg_2SO_4 + 2H^+ + 2e$
+0.666	$Pb + 2\,H_2O \rightleftharpoons PbO_2 + 4H^+ + 4e$
+1.100	$PbO + H_2O \rightleftharpoons PbO_2 + 2H^+ + 2e$
+1.230	$2H_2O \rightleftharpoons O_2 + 4H^+ + 4e$
+1.58	$Pb + PbO_2 \rightarrow 2\,PbO$ Voltage Limit
+1.684	$PbSO_4 + 2H_2O \rightleftharpoons PbO_2 + H_2SO_4 + 2H^+ + 2e$

Fig. 1 - Standard electrode potentials for some electrochemical reactions of lead and other reactions

The reaction $Pb + H_2SO_4 \overset{2e}{\rightleftharpoons} PbSO_4 + 2\,H^+$ at the E^0 value -0.355 is the reaction which occurs at the negative plate of the lead-acid cell. It has nothing to do with the corrosion process occurring at the positive plate of a battery, and it is given in Fig. 1 for orientation purposes only. In a constant-current anodization process, however, it would be the first reaction to occur.

The oxidation of Pb to PbO (or $Pb(OH)_2$) has been shown to occur at potentials more noble than +0.252,[1,4] and PbO (tetragonal) was found to be the principal reaction product up to potentials approaching that for the reversible reaction at the positive plate.[1] Theoretically, this product is not stable at these potentials, being subject to chemical attack by the acid to form $PbSO_4$. Evidently, however, the resulting $PbSO_4$ coating effectively excludes the $SO_4^=$ ion from the underlying PbO film. The fact that the production of PbO occurs very near its reversible potential indicates that the film is porous; otherwise an appreciable overvoltage might be expected. At more noble potentials, the next reaction which can occur is the direct oxidation of Pb to PbO_2 by water, E^0 = +0.666 volt; and if the film is porous it would be expected to occur. It is to be noted that PbO_2 formation is possible at a potential a full volt below the reversible positive-plate potential. However, it is not stable below that potential, tending to react at the solution interface with H_2SO_4 and H^+ to give $PbSO_4$ and PbO, and at the metal interface to give PbO by means of the solid-phase reaction. Above the potential +1.100, corresponding to the reaction $PbO + H_2O \overset{2e}{\rightleftharpoons} PbO_2 + 2\,H^+$, the PbO_2 would no longer be unstable due to reaction with H^+ to form

PbO, but would still be unstable on both the other counts. The fact that above the voltage +1.100 PbO is found to be the chief product[1] indicates that either the reaction proceeds by direct oxidation of Pb to PbO or by oxidation of Pb to PbO_2 followed by the solid-phase reaction. The possible reaction $PbO + H_2O \rightleftharpoons PbO_2 + 2H^+ + 2e$ does not go to any appreciable extent; otherwise either PbO_2 would be found in the reaction product or $PbSO_4$ would be the chief product. Yet, x-ray analysis indicates only $PbSO_4$ and PbO, and the data show correspondence with Faraday's law for the reaction $Pb \rightarrow Pb^{++} + 2e$.

Considering more noble potentials, if the primary reaction is direct oxidation of Pb to PbO_2, then PbO_2 should begin to be found in the reaction product as the potential passes the value +1.58. It should occur along with $PbSO_4$, PbO no longer being present. Finally, above the reversible $PbO_2/PbSO_4$ potential, PbO_2 should be the sole solid product.

KINETIC THEORY

The kinetics of the possible processes will next be considered in order to get an idea as to possible factors which could control corrosion rates.

If the film is continuous and stays so, either one of two possible rate laws may apply, i.e.,

$$w = Bt \tag{1}$$

$$w^2 = kt \tag{2}$$

depending on whether the rate is limited by reaction at one of the film interfaces[5] or by migration of ions through the film.[6] In these equations, w is the film weight, B and k are constants, and t is time. In Eq. 2 the constant k contains the potential existing across the film to the first power; so that at constant time the relation between w and potential should also be parabolic.

Evans has considered mechanical breakdown of films growing in gaseous media and has shown that if breakdown of an adherent film produces cracks too fine to allow the oxidizing medium to reach the metal surface, migration of ions along the cracks should take place at an enhanced rate.[7] Then the parabolic law would be retained, but at higher rates. On the other hand, if compressional stresses in the film should result in blistering, and the walls of the blisters crack, the oxidizing medium may be admitted to the cavity in bulk, and the growth over relatively long periods should obey a linear law. If the blister walls are impervious to the oxidant then the flat cavities constitute barriers to migration through the film and the following logarithmic relationship results

$$w = k_1 \log (k_2 t + k_3). \tag{3}$$

In this case it may be noted that breakdown results in a lower rate than the continuous film would provide.

When cracking sufficient to admit the oxidant to the metal surface occurs in electrochemical systems, several possibilities appear to exist. First, if the intrinsic rate of the reaction at the metal surface is controlling, then the rate will be given by the usual equation

$$\text{rate} = k \times a_A^n \times a_B^n \times \cdots \tag{4}$$

where k is the specific reaction velocity constant and a_A and a_B are the activities of the reacting species. Where a film is formed and A is the metal surface, then a_A may be considered equivalent to the area of metal exposed at the bottoms of pores. This should be large at zero time and fall off rapidly as the film spreads across the surface. By the

time it begins to grow in depth the process of cracking might be expected to result in a constant pore area; if so, then the rate would become constant with time, and w would be given by the equation

$$w = k'A\, a_B^n \times - - - xt \tag{5}$$

where A is the pore area. Conformance of a process to this type would indicate a low specific rate constant, low enough so that rates would not be limited by diffusion.

If the electrode process were characterized by an overvoltage, an equation of the type previously derived (Ref. 1, Eq. 6) would apply. For conditions of constant area this would become

$$w = kA\, e^{k'V} t \tag{6}$$

and film growth would be linear with time at constant voltage, and exponential with voltage at constant time.

Where the specific rate constant is large and the reaction has no overvoltage, diffusion of electrolyte through the pores of the film may be expected to be the rate-limiting process. For a constant pore area, A, the diffusion current would be given by

$$I = \frac{kAD\,(c_o - c_i)}{l} \tag{7}$$

where D is the diffusion constant and $c_o - c_i/l$ the concentration gradient of the diffusing reactant. Through Faraday's law and because l is simply related to w, the relation

$$w^2 = k'AD\,(c_o - c_i)\,t \tag{8}$$

may be obtained.

Film growth might also be limited by the resistance of the electrolyte in the pores of the film. In this case,

$$I = \frac{VA}{\rho l} \tag{9}$$

where V is the IR drop across the pores and ρ is the specific resistance of the electrolyte in the pores. At constant A and V,

$$w^2 = \frac{kAV}{\rho} t \tag{10}$$

and again the relation is parabolic. In this case, rate is a linear function of potential at constant film thickness.

Evidently, there are several mechanisms that can each lead to parabolic and linear w vs. t relationships; so that for data which fit either form, the form is not sufficient to characterize the mechanism. If possible, choice amongst mechanisms would have to be made on the basis of the constants of the equations. This could be difficult, owing to lack of knowledge of the values of some of these constants, such as pore area.

EXPERIMENTAL WORK

The method, apparatus, and techniques employed have been described previously.[1] Single samples were used for voltages below the $PbO_2/PbSO_4$ reversible potential and these were generally corroded for times up to about 72 hours. Corrosion current was recorded, the films were stripped, and weight losses were determined. The results were then checked against Faraday's law.

For rate determinations above the $PbO_2/PbSO_4$ reversible potential, longer times were necessary to enable an estimate of the rate; furthermore, some of the current went to O_2 gas, so that current measurements and Faraday's law could not be used to obtain estimates of the rate. Consequently, four or five samples were used. These were removed one at a time over the course of a week or so, stripped in an alkali-hydrazine-mannitol bath, and weight-loss determined. The results were plotted against time, and the slopes of the curves measured to get rates.

All potentials were measured against a mercurous sulfate mercury reference electrode in the electrolyte of the anodizing cell.

X-ray analysis of the films were made under certain conditions to determine the nature of the corrosion products.

DATA

Corrosion-rate curves at room temperature for relatively short times were obtained at potentials ranging from about 0.2 volt below the $PbO_2/PbSO_4$ reversible potential to about 0.05 volt above, in acid strengths of 1%, 10%, 30%, and 40% by weight. Weight losses were obtained for these samples by stripping to check against those calculated from Faraday's law. In Figs. 2, 3, 4, and 5 are shown several current-time curves for each acid concentration to illustrate the effect of potential.

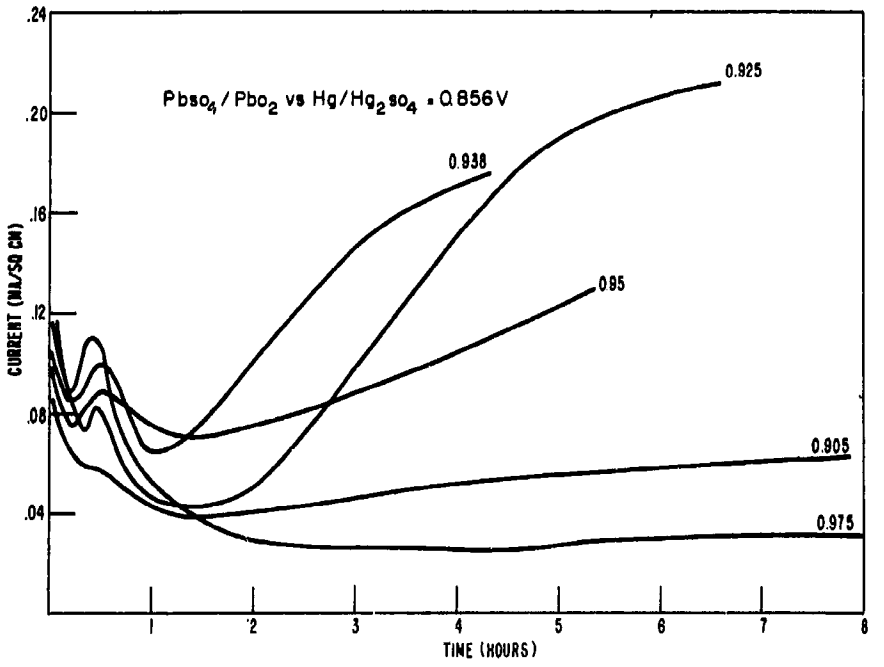

Fig. 2 - Corrosion current vs. time.
1% acid at several potentials

Table 1 shows the final weight-loss data for these runs, from which an estimate of the distribution of the current between divalent and tetravalent products was made. The table also includes the results of the x-ray examination of particular samples. The bulk of any $PbSO_4$ formed was always in the outer layer of the film. It was porous and nonadherent, and could be wiped off with a cloth.

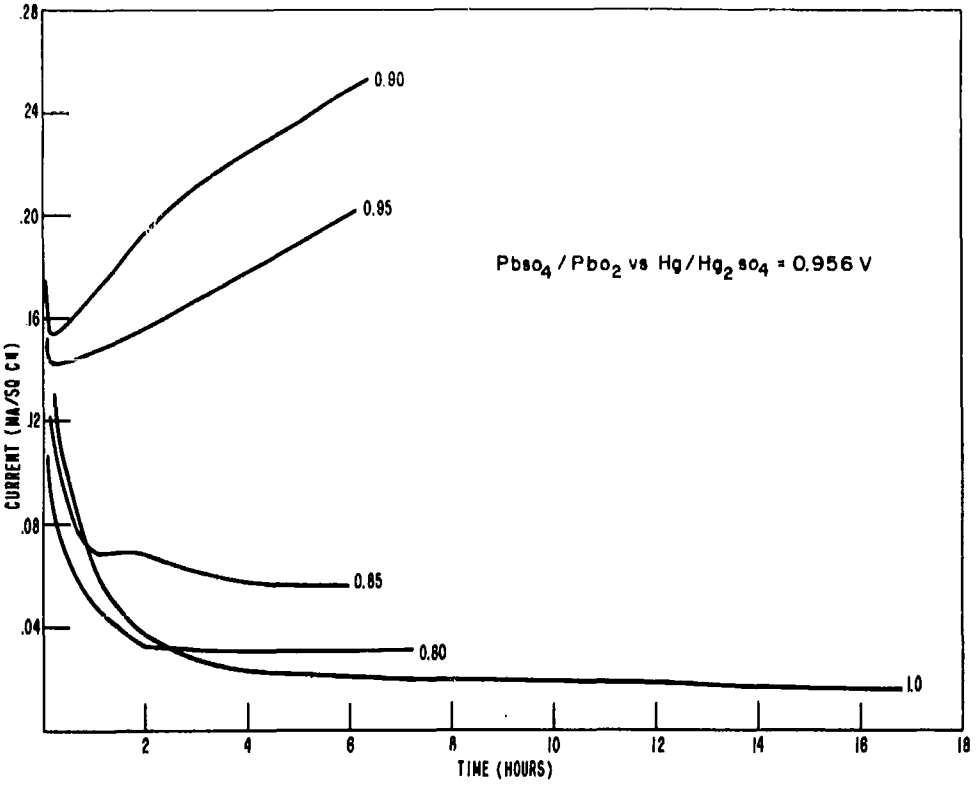

Fig. 3 - Corrosion current vs. time. 10% acid at several potentials

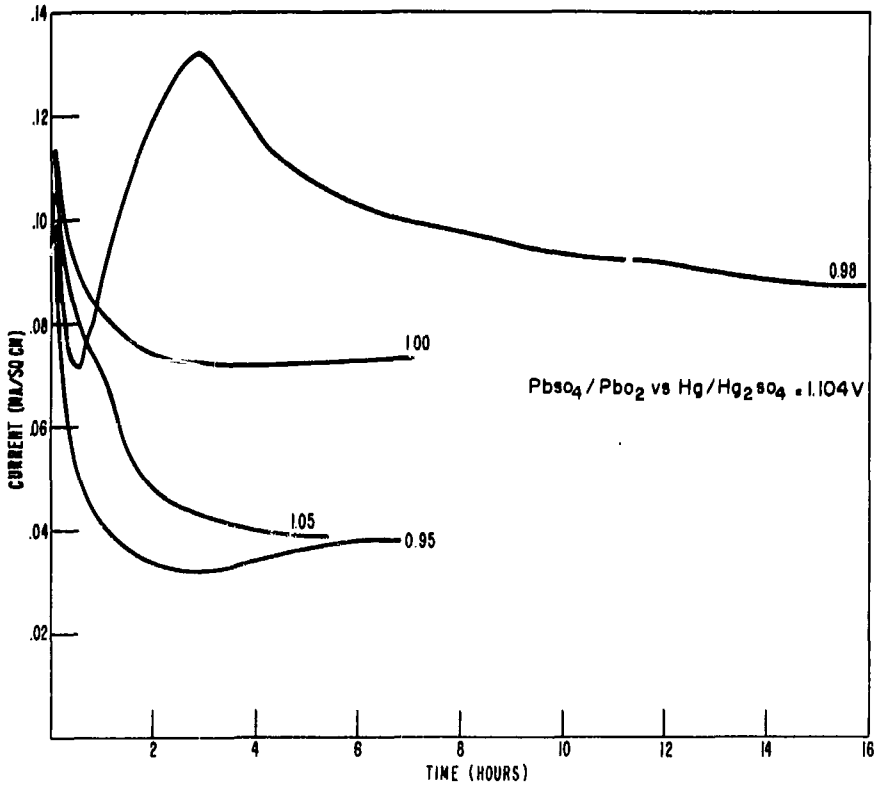

Fig. 4 - Corrosion current vs. time. 30% acid at several potentials

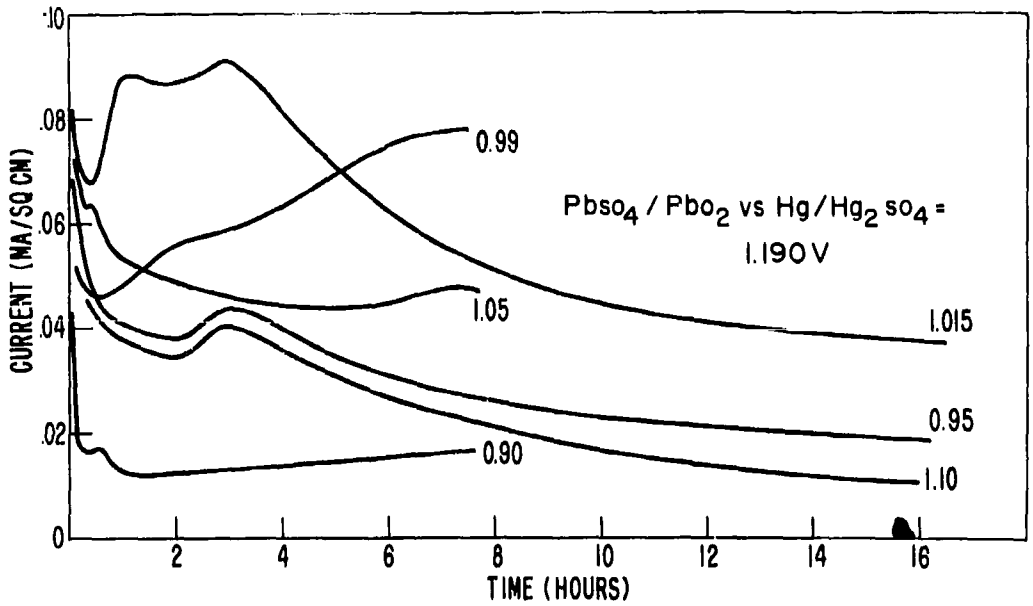

Fig. 5 - Corrosion current vs. time. 40% acid at several potentials

TABLE 1
Corrosion Data Near the $PbO_2/PbSO_4$ Potential

% Acid Concentration	Voltage	Weight Loss from Faraday's Law Calc'd for: $Pb \rightarrow Pb^{2+}$ (mg/sq cm)	Weight-Loss Found (mg/sq cm)	% of Current to Divalent Products	Film Analysis by X-ray
1	0.905	1.53	1.51	98	PbO, $PbSO_4$
	0.925	3.13	3.00	91	
	0.938	1.92	1.76	84	
	0.950	1.67	1.63	95	
	0.975	1.13	0.97	75	$PbSO_4$, PbO_2
10	0.80	1.24	1.25	100	PbO, $PbSO_4$
	0.85	1.41	1.35	92	
	0.90	3.34	3.25	95	
	0.95	3.34	3.20	92	
	1.00	2.09	1.70	65	$PbSO_4$, PbO_2
30	0.95	1.07	1.10	100	PbO, $PbSO_4$
	0.98	3.38	3.20	90	
	1.00	2.14	1.90	79	$PbSO_4$, PbO, PbO_2
	1.05	1.24	1.10	80	
	1.115*				PbO_2, $PbSO_4$
	1.125*				PbO_2, ($PbSO_4$)
40	0.90	0.52	0.55	100	PbO, $PbSO_4$
	0.95	1.86	1.82	78	
	0.99	1.92	1.85	94	PbO, $PbSO_4$
	1.015	3.60	2.74	53	
	1.05	1.41	1.14	60	
	1.10	1.48	1.15	53	PbO_2, $PbSO_4$

*Data from Fig. 13

Figures 6, 7, 8, and 9 show the weight-loss as a function of time calculated or estimated from the current curves. When the products consist of 100% bivalent lead compounds, the weight-loss curves are exact within experimental error. But, if some PbO_2 is present, only the final weight-loss is exact because weight losses between the beginning and the end were estimated from the current curves on the assumption that the fraction of the current which produced divalent products was constant with time. This is not always correct, as will be shown; nevertheless the weight-loss curves do give a good idea of the effect of potential.

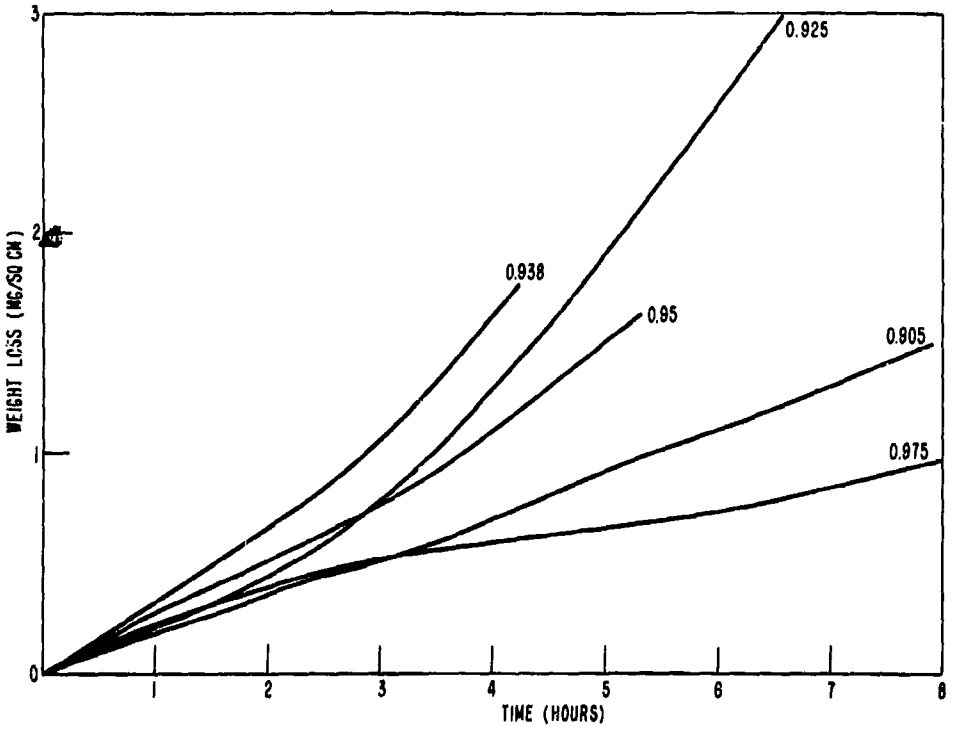

Fig. 6 - Current data from Fig. 2 converted to weight loss

The weight-loss data taken above the $PbO_2/PbSO_4$ reversible potential under several conditions of concentration and temperature are shown in Figs. 10, 11, and 12. At these potentials PbO_2 was, as expected, found to be the only corrosion product whenever the film were thick enough to allow analysis.

To obtain the corrosion rate-voltage relationship in still finer detail just above the $PbO_2/PbSO_4$ potential, additional runs were made in 30% acid at 1.115 and 1.125 volts. The data are shown in Fig. 13. Data are included from Figs. 8, 11, and 16 for comparison. This set of curves suggested the possibility of an inflection in the rate vs. potential curve at potentials just below the reversible $PbO_2/PbSO_4$ potential; so it was decided to study this range in detail for 30% acid. In this case single samples were run for various times at a constant potential and stripped to obtain weight loss. Current was measured vs. time to enable the effect of time on the distribution of products between di- and tetravalent compounds to be determined. The data, at room temperature, are shown in Figs. 14 through 17.

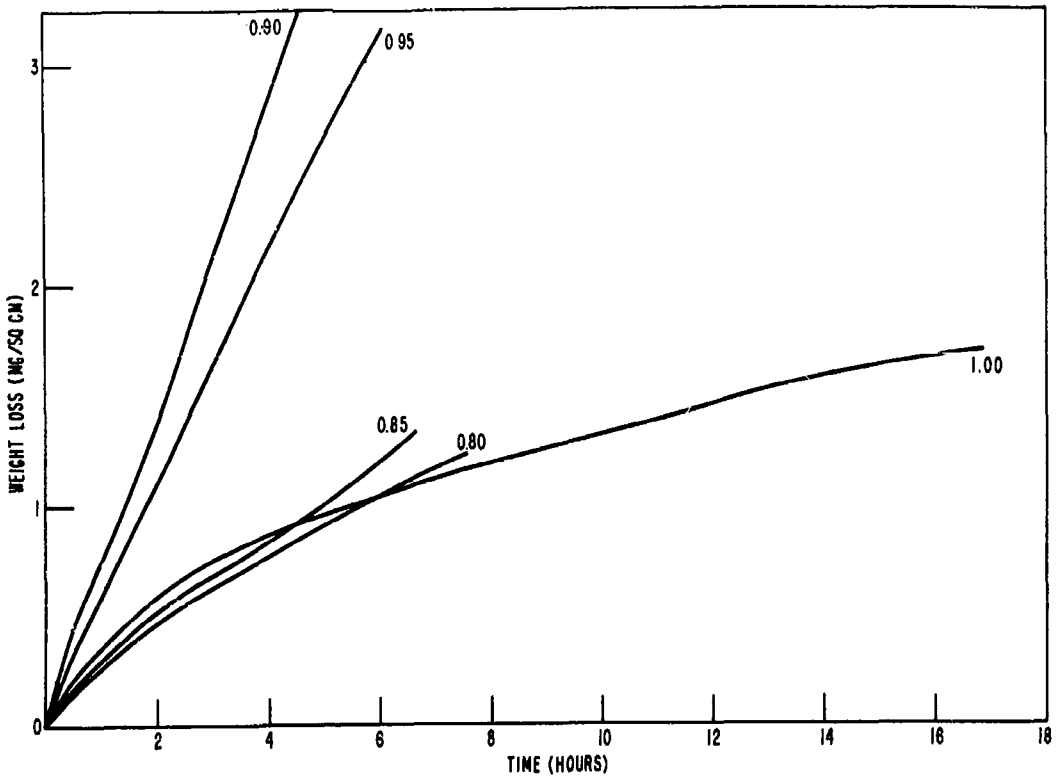

Fig. 7 - Current data from Fig. 3 converted to weight loss

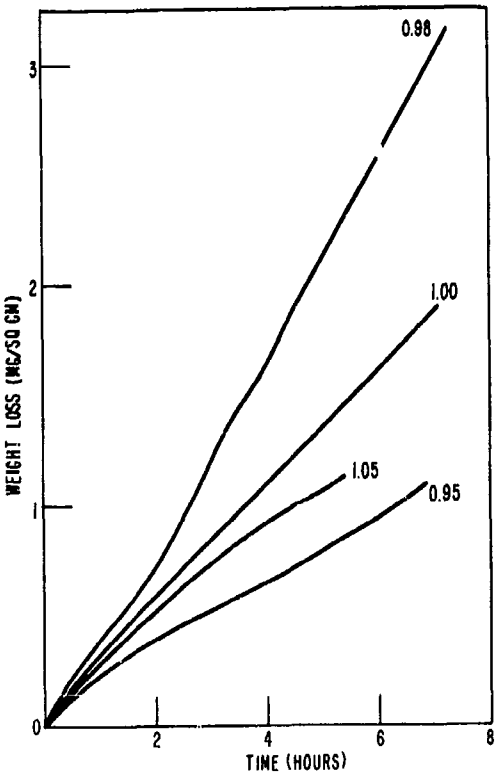

Fig. 8 - Current data from Fig. 4 converted to weight loss

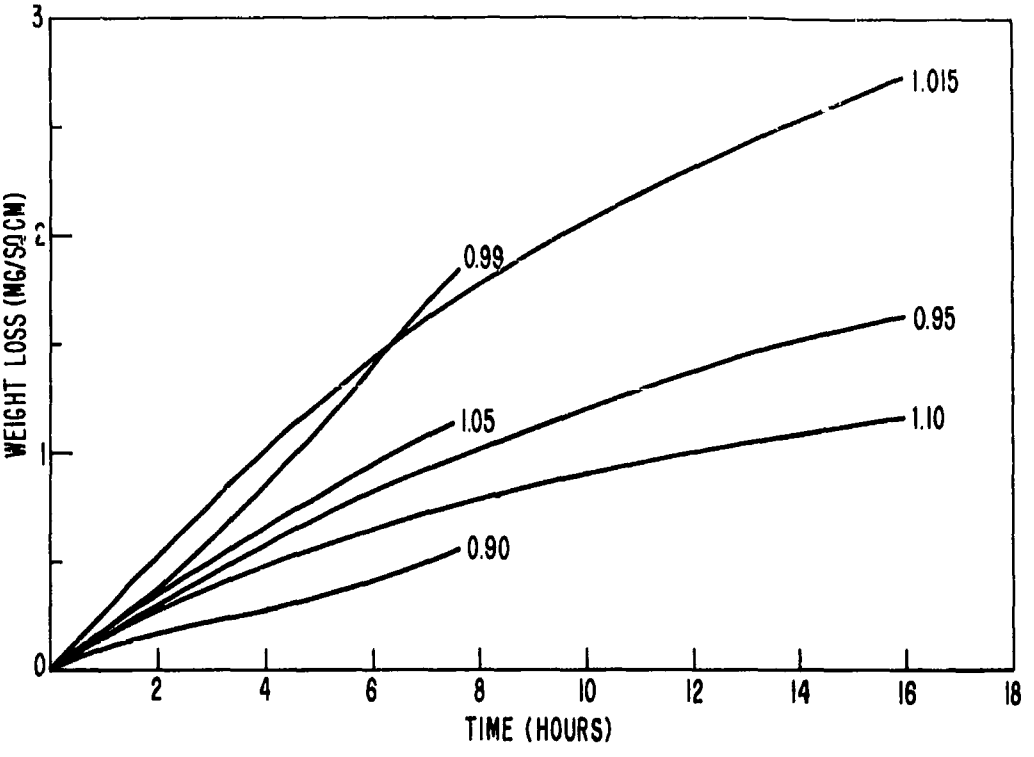

Fig. 9 - Current data from Fig. 5 converted to weight loss

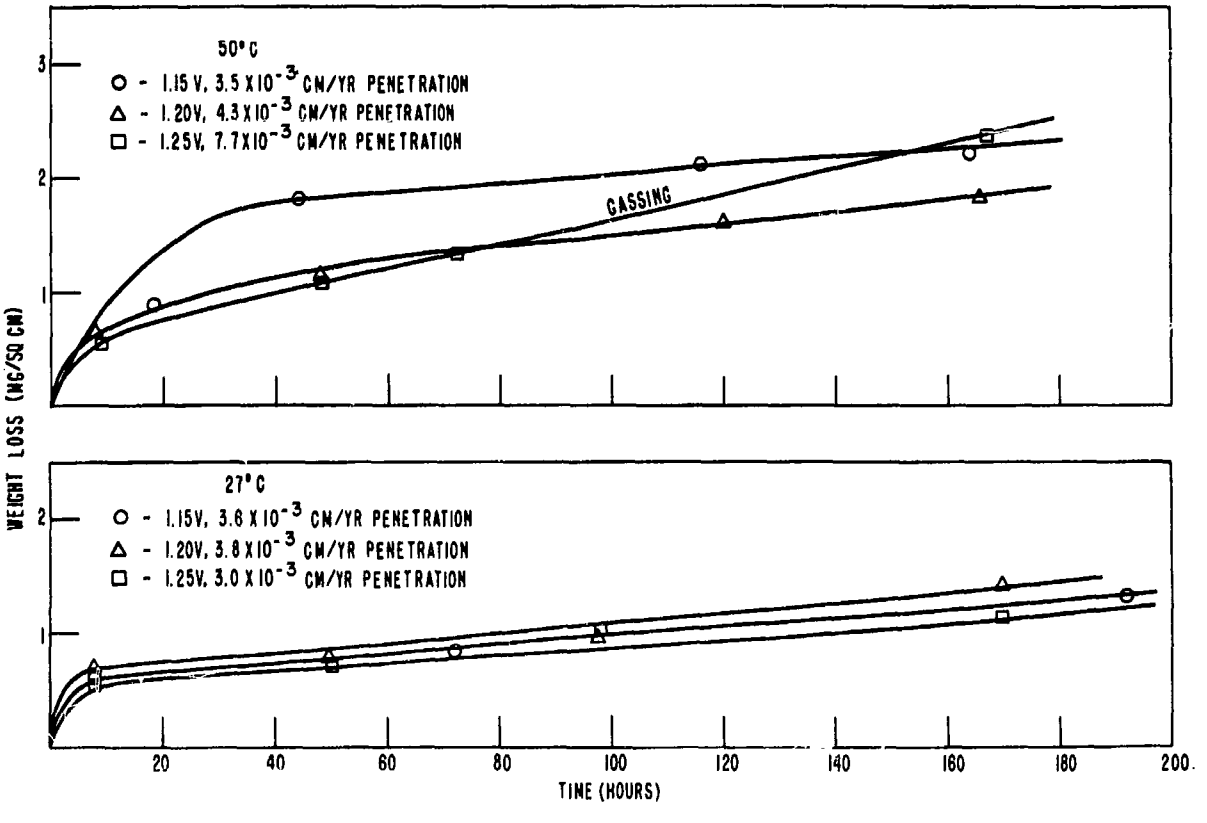

Fig. 10 - Corrosion above the $PbO_2/PbSO_4$ reversible potential with 10% acid

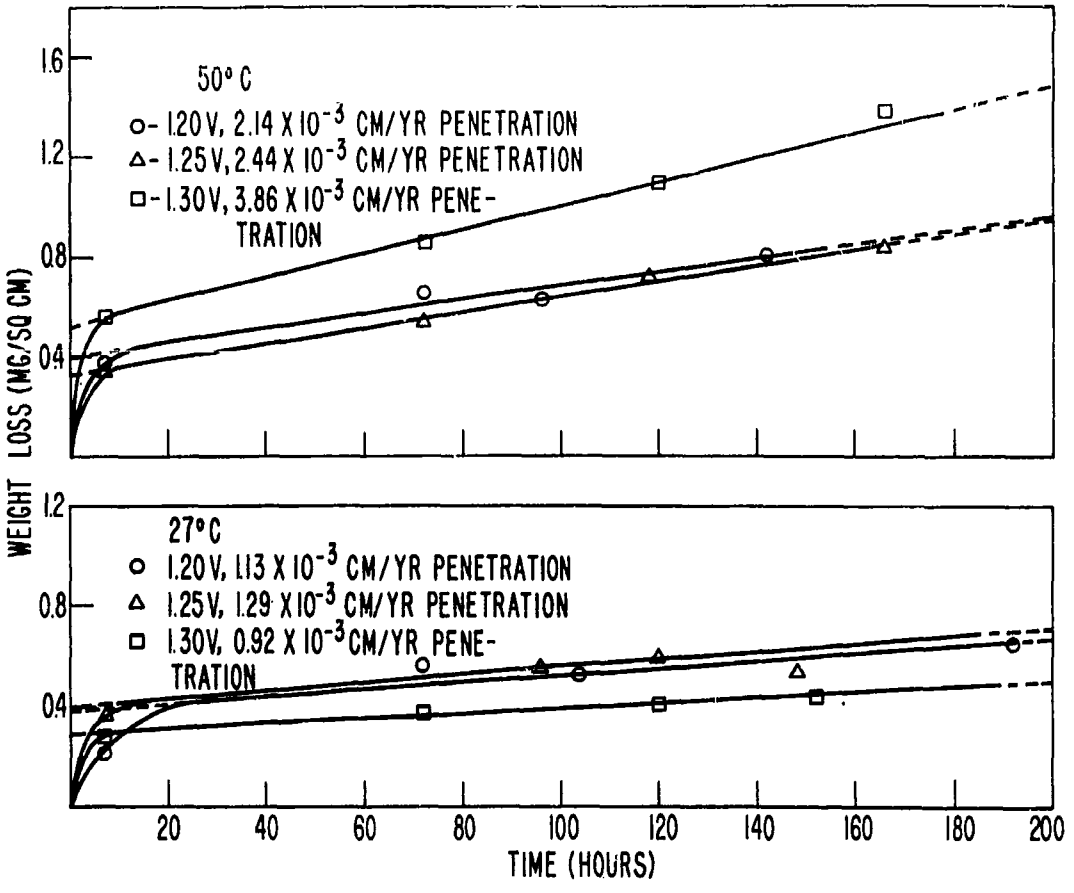

Fig. 11 - Corrosion above the $PbO_2/PbSO_4$ reversible potential with 30% acid

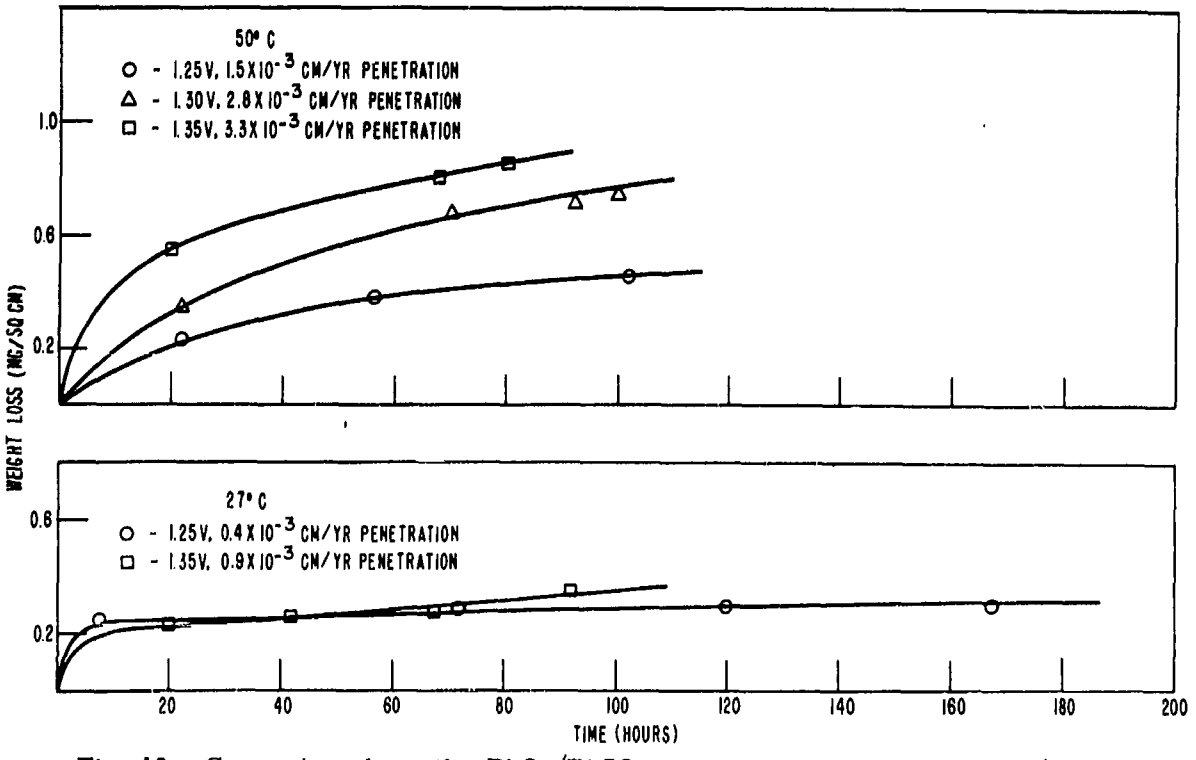

Fig. 12 - Corrosion above the $PbO_2/PbSO_4$ reversible potential with 40% acid

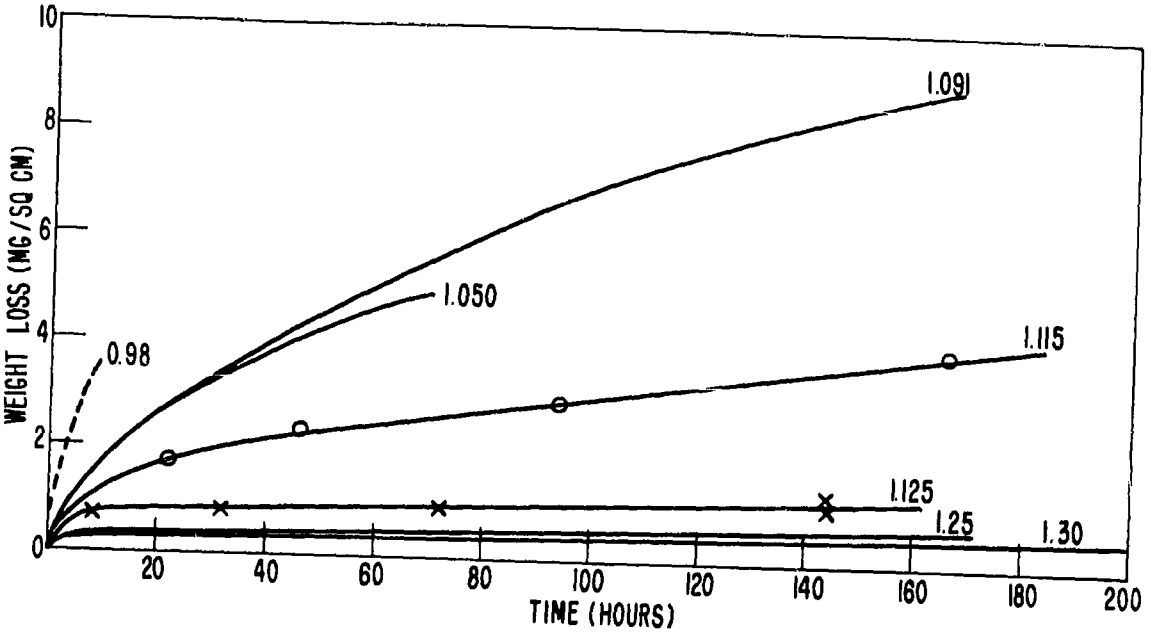

Fig. 13 - Corrosion in 30% acid, at several potentials

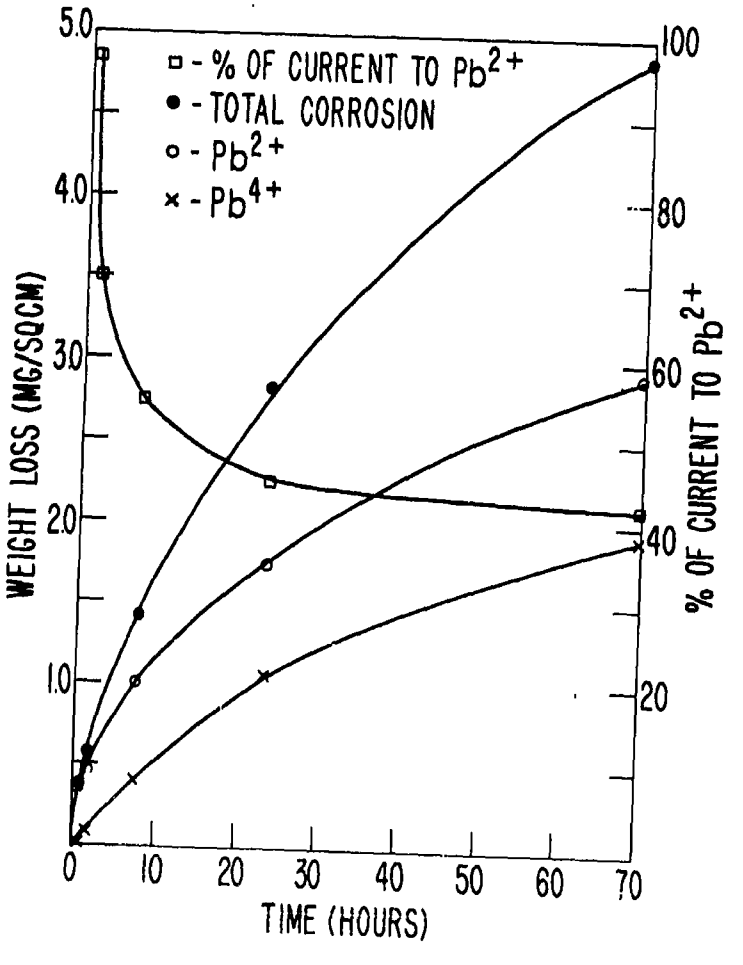

Fig. 14 - Total corrosion and distribution of corrosion products with 30% acid at 1.050 volts

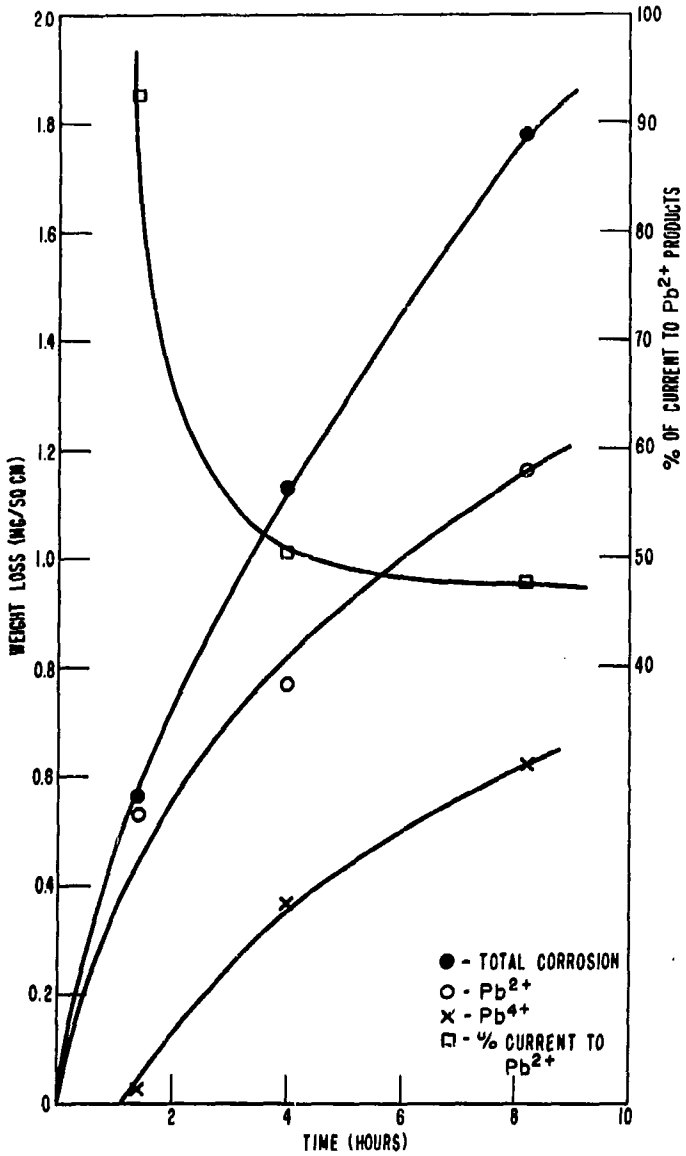

Fig. 15 - Total corrosion and distribution of corrosion products with 30% acid at 1.075 volts

THE CORROSION PROCESS BELOW THE POTENTIAL OF THE RATE PEAK

Combining the data of the present paper and that available from the previous work,[1] a plot of corrosion rate vs. potential may be made over the range -0.134 to +1.30 volts. This has been done for 30% acid at a constant weight loss of 1.18 mg/sq cm at room temperature. The result is shown in Fig. 18. The reaction products found over the various potential ranges are also shown. Actually, for a cell in any kind of service from cycling to float, the voltage range below some potential in the neighborhood of the peak in the curve is not of interest in the practical corrosion problem, because rates are not controlled by the same mechanism on either side of the peak and because voltages (even in a cycling cell) do not drop below the voltage of the peak, except perhaps on a deep discharge or a high-rate discharge. However, the chemistry is interesting and since it is believed that an erroneous mechanism of corrosion was suggested previously,[1] some consideration will be given to this voltage range. The data of the previous report will be used to elucidate what is now considered to be the proper mechanism.

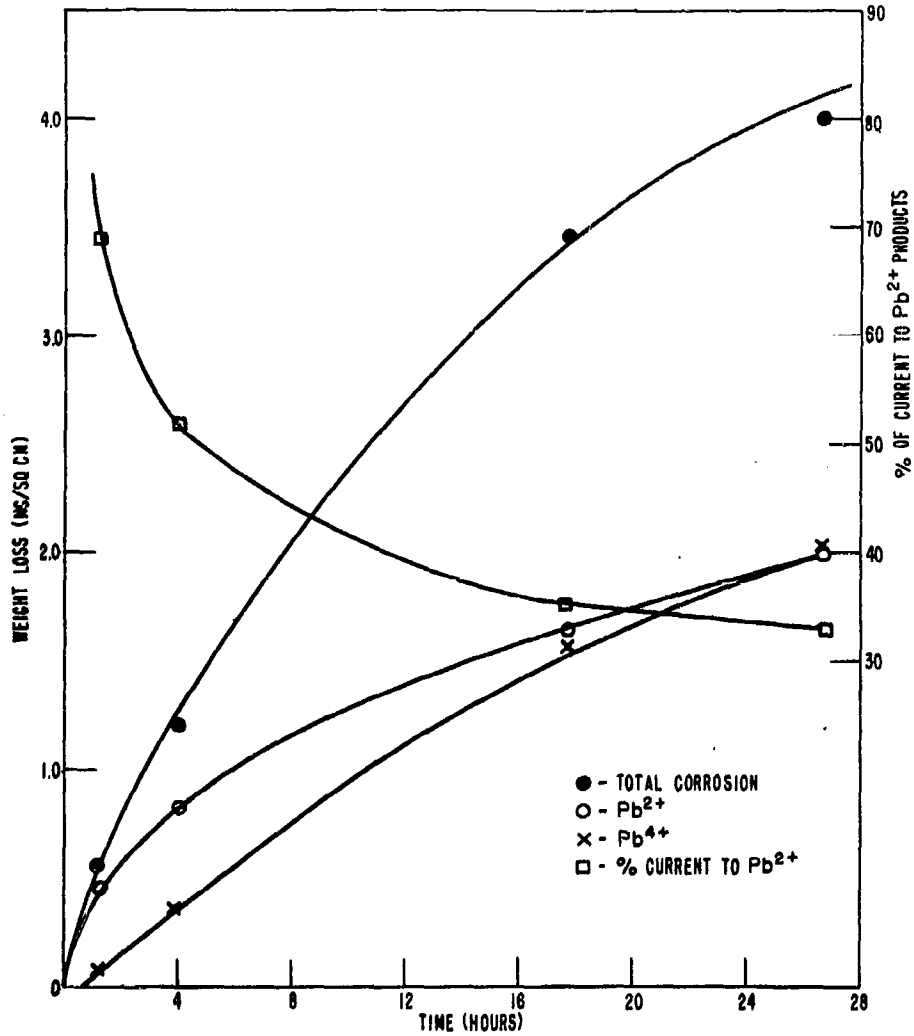

Fig. 16 - Total corrosion and distribution of corrosion products with 30% acid at 1.090 volts

The treatment of the data is as follows: a constant amount of corrosion (weight loss) may be selected and the corresponding corrosion rate plotted vs. potential. This has been done using the data of Figs. 5 to 12 of the previous report.[1] The results are shown in Fig. 19 of this report for a weight loss of 1.47 mg/sq cm at 30° and 50°C with 10% and 30% acid. The linearity of these curves suggests that the rate is limited by the resistance of the PbO film which is formed next to the metal surface.[1]

From the data of Fig. 19, it is indicated that a break in the curve occurs close to the reversible potential for the reaction $Pb + 2H_2O \overset{4e}{\rightleftharpoons} PbO_2 + 4H^+$. This break is more sharply defined in similar data collected for a 0.05 molar acid at room temperature as shown in Fig. 20. Furthermore, a change in reaction or mechanism is indicated by the data of the previous report (Ref. 1, Figs. 13 and 14) by the fact that in the neighborhood of this potential the slopes of the log w vs. log t curves change from 0.55 to 0.61 — 0.88, as potential increases. This is taken as indirect evidence that PbO_2 formation does, in fact, begin very near its reversible potential. It does not appear as a reaction product, however, because it is unstable on the three counts listed in the theoretical discussion.

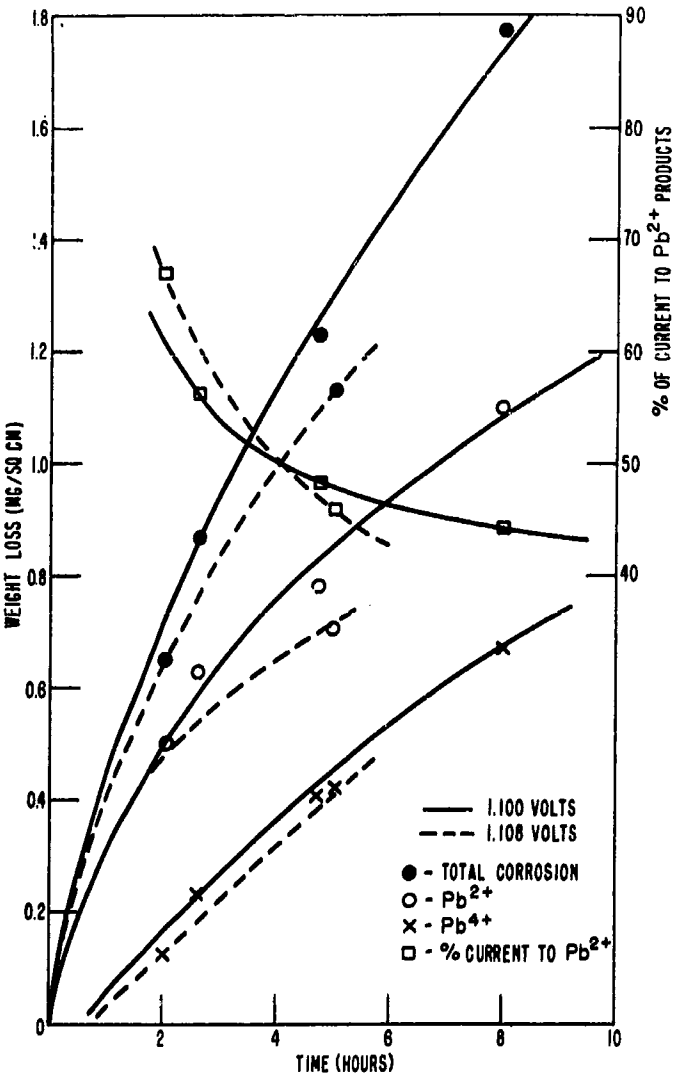

Fig. 17 - Total corrosion and distribution of corrosion products with 30% acid at 1.100 and 1.108 volts

On this basis, the corrosion process is considered to be driven by the difference in the reversible potentials between the anodic reaction, $Pb + 2\,H_2O \overset{4e}{\rightleftharpoons} PbO_2 + 4H^+$, and the cathodic reaction, $PbO_2 + H_2SO_4 + 2H^+ \overset{2e}{\rightleftharpoons} PbSO_4 + 2H_2O$. Since the difference in potential between the polarized corrosion sample and the reversible potential for the PbO_2 formation reaction represents chiefly IR drop across the PbO film, the film resistance may be calculated from Ohm's law, or better, from the slopes of the curves of Fig. 19. The curves are displaced vertically for different acid concentrations because of different residual currents corresponding to PbO formation at lower voltages.

It is still questionable whether or not the film is porous, i.e., whether the reaction is proceeding by migration of ions through a solid, continuous film, or whether the reaction takes place at the metal-solution interface at the bottoms of pores. In either case, the relation between w and t should theoretically be parabolic (Eqs. 2 and 10), but in this case w should increase with some power of t greater than 0.5, because the film is being converted on the outside by chemical action to a loose coat of $PbSO_4$. Values of this power of t have been found to range between 0.6 to 0.9.[1] A difference between the two mechanisms might allow a choice: if the film is continuous, the resistance of the film is the resistance of a solid coat of PbO and the area term in the equation is the

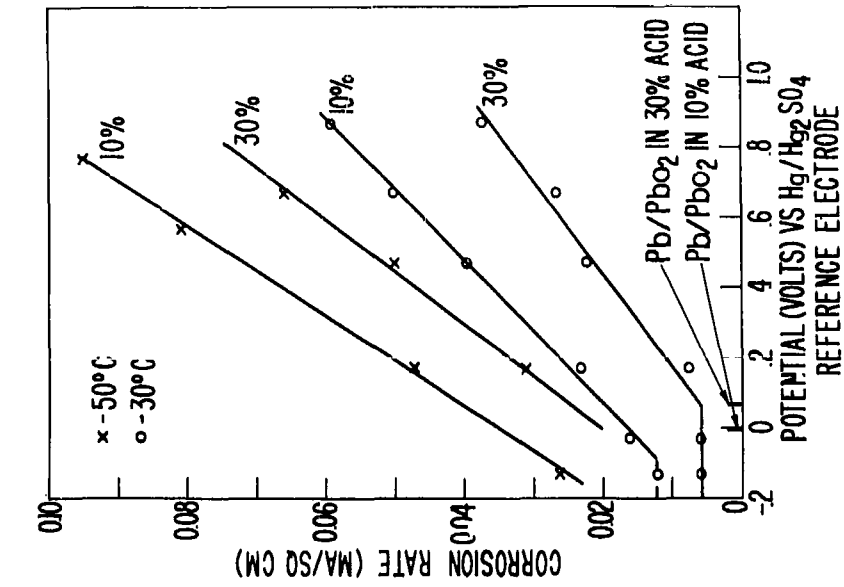

Fig. 19 - Corrosion current vs, potential, PbO range, at a constant weight loss of 1.47 mg/sq cm

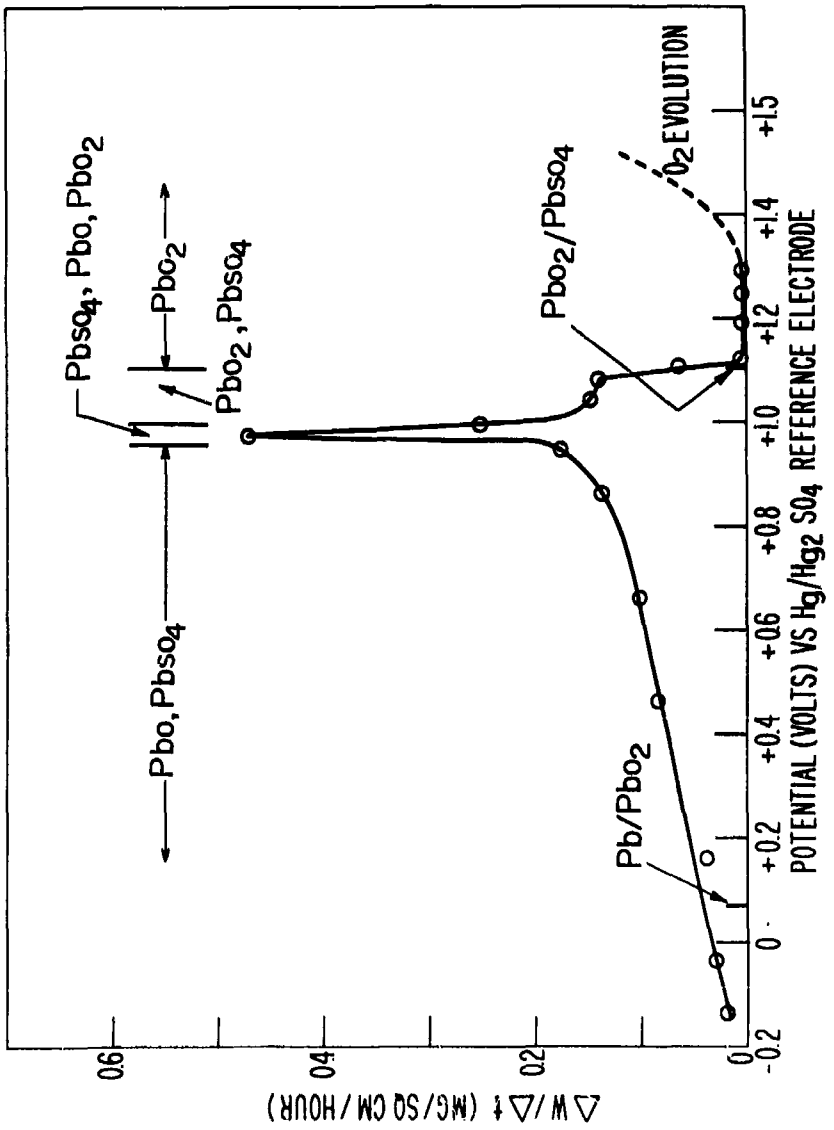

Fig. 18 - Corrosion rate vs. potential in 30% acid at a constant weight loss of 1.18 mg/sq cm (10,000 A)

gross area of the sample; if the film is porous, the resistance is the resistance of the electrolyte in the pores and the area term is the total pore area. For a continuous film, the resistance may be expected to decrease exponentially with temperature by comparison with the theory of dry, high-temperature oxidation.[7] For a porous film on the other hand, the decrease in resistance with temperature would correspond to the known decrease of the acid involved.

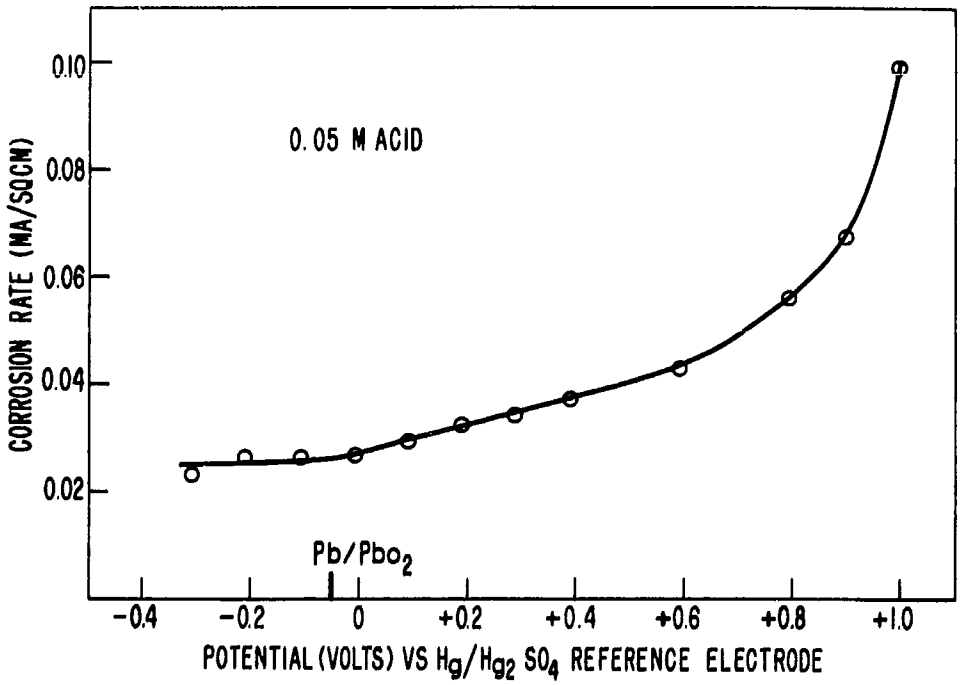

Fig. 20 - Corrosion current vs. potential, PbO range, at a constant weight loss of 1.47 mg/sq cm

From the slopes of the curves in Fig. 17 the resistance of 1 sq cm of the film has been calculated with the results shown in Table 2. Enough temperature data is not available to determine whether the rate increases logarithmically with 1/T, but if it is assumed that the data for the two temperatures does follow such a plot, the activation energy may be determined to be 9000 cal per mole. High-temperature oxidation studies for other metals show values ranging from 30,000 to 54,000 cal per mole.[7] Consequently, it may be concluded that corrosion rates are not limited by a continuous film. The ratios of resistances of these electrolytes at 30° and 50°C are 1.25 and 1.32 for the 10% and 30% acids, respectively. The ratios in resistance of the experimental films are 1.58 and 1.68, respectively. The agreement might be good enough when it is considered that comparison was made at constant weight loss, while the equation demands comparison at constant film thickness. However, the higher temperature might speed up the chemical reaction which converts PbO to $PbSO_4$ in comparison with the PbO-producing reaction, which would result in a lower effective value of film thickness at the higher temperature, causing the experimental ratios, calculated above, to be too high. A similar effect might be involved in the area term.

Although the film may be considered to be porous, it might well be described as a tight, porous film because estimates can be made of the pore area from the gross value of resistance found experimentally and the specific resistance of the solution. These

estimates give values of about 1×10^{-8} sq cm/sq cm of gross surface, depending on the effective path length of the pores. The value would be larger if the film cracked or blistered in such a way as to render the paths of the pores tortuous.

TABLE 2
Resistances of PbO Films

% Acid	30°C	50°C
10	$2.02 \times 10^4 \Omega$/sq cm	$1.28 \times 10^4 \Omega$/sq cm
30	$2.66 \times 10^4 \Omega$/sq cm	$1.48 \times 10^4 \Omega$/sq cm

THE CORROSION PROCESS AT THE POTENTIAL OF THE RATE PEAK

Next, the narrow potential range covering the tremendous peak found in the rate curve below the $PbO_2/PbSO_4$ potential, as illustrated for 30% acid in Fig. 18, will be considered. The data concerned are included in Figs. 2 through 9, and in Table 1. If the rate of corrosion ($\Delta w/\Delta t$) at a constant weight loss of 1.18 mg/sq cm is plotted against potential measured with respect to the Hg/Hg_2SO_4 reference electrode in the same solution, the set of curves shown in Fig. 21 is obtained. The estimated percent of current which forms divalent products is given by the number next to each point. Evidently, as voltage is increased, the steep rise in the rate curve begins when PbO_2 begins to be found in the reaction products. It is not found in quantity, however, until the peak is passed and rates fall off sharply.

There are several features of these curves to which attention may be directed. First, the peaks do not appear to have anything to do with the location of the reversible $PbO_2/PbSO_4$ potential, being found below it in stronger acids and above it in weaker acids. Second, the chief products of reaction on the low-voltage side of the peak are PbO and $PbSO_4$, except when the high-voltage side is above the reversible potential; then they are PbO and PbO_2 (1% and 10% acid). Third, in the case of the 1% acid the chief reaction product continues to be PbO for almost a tenth of a volt beyond the reversible $PbO_2/PbSO_4$ potential. Fourth, as shown in Fig. 22 the position of the peak falls at the same potential, regardless of acid strength, when rate is plotted against potential referred to the standard hydrogen electrode; in other words, the position of the peak does not vary with voltage.

It has been shown in earlier work that PbO_2 undergoes a solid-phase reaction with lead to form PbO, and it was suggested at that time that on discharge the PbO_2 formed during the previous charge underwent the solid-phase reaction with the grid metal to produce an intermediate film of PbO.[3] It is now believed that the maximum in the corrosion rates, illustrated in Figs. 21 and 22, actually corresponds very nearly to the voltage beyond which such a solid-phase reaction will not occur, because the lead becomes so highly positively charged that the PbO_2 hasn't the power to take away electrons—as discussed in the theory. Although no direct evidence is available to prove this, it seems to fit in with the experimental data, * especially the two facts that the potential of the peak does not vary with concentration, and that PbO is the chief reaction product in 1% acid at voltages beyond the reversible $PbO_2/PbSO_4$ potential.

*Additional evidence is given by unpublished NRL data which shows that a 4-1/2% tin alloy of lead does not exhibit the peak in the rate curve. This alloy does not undergo the solid-phase reaction, except perhaps at very low rates.

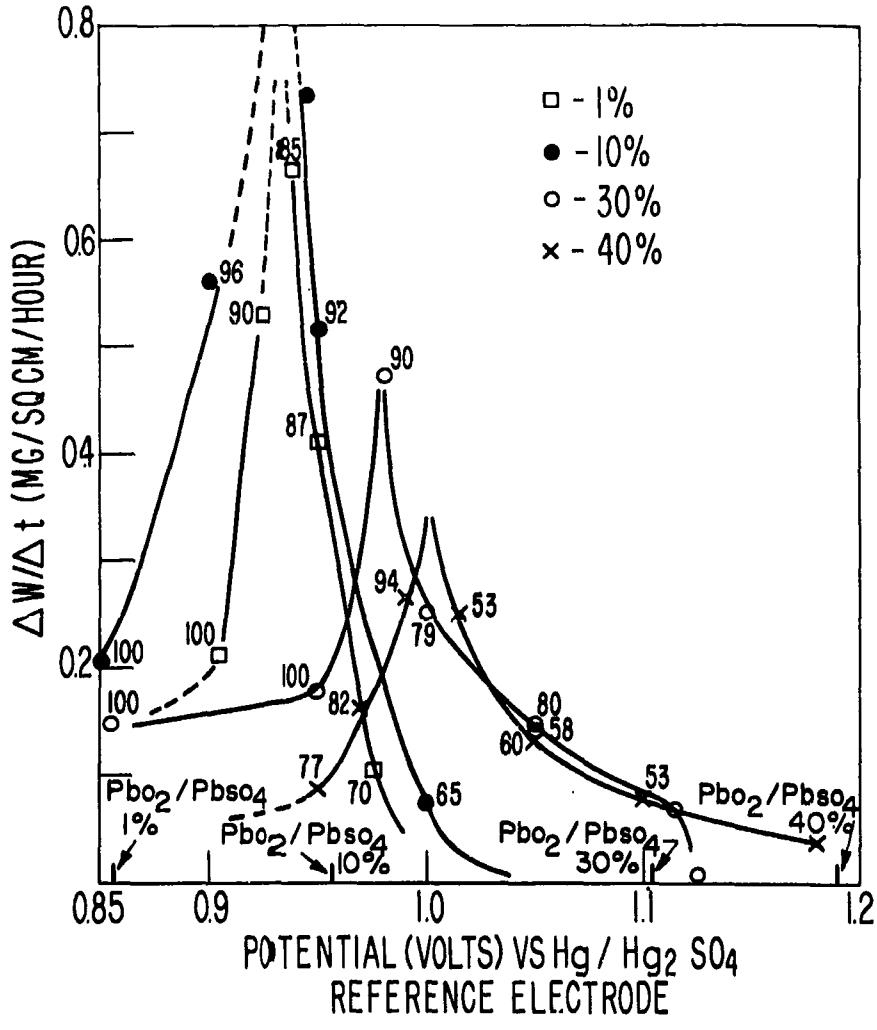

Fig. 21 - Rate of corrosion vs. potential for several acid strengths at a constant weight loss of 1.18 mg/sq cm

The picture now seems clear: PbO_2 is formed in the initial corrosion reaction at the metal surface at voltages considerably below the $PbO_2/PbSO_4$ potential; it is unstable, reacting by the solid-phase reaction at the lead-oxide interface to form PbO, and being reacted upon by the solution to produce $PbSO_4$ and PbO below the PbO/PbO_2 voltage. Above the latter voltage only the solid-phase reaction and the normal positive-plate discharge reaction are available for forming divalent products. Above the PbO/PbO_2 potential, PbO would not be expected to appear as a reaction product unless the solid-phase reaction occurs; yet it is found to be the chief product. As potential is increased still further, PbO_2 begins to appear in the product when the voltage becomes too high for the solid-phase reaction to go, the PbO film is broken down and rates are no longer controlled by the highly resistant PbO film.

If it is true that the potential of the peak corresponds to the limit of the solid-phase reaction, then two interesting conclusions may be drawn — one of theoretical interest, the other of more practical interest. First, if the solid-phase reaction is limited because PbO_2 can no longer take away electrons from the highly positively charged metal, it is suggested that the positive charge on the grid counterbalances the free energy

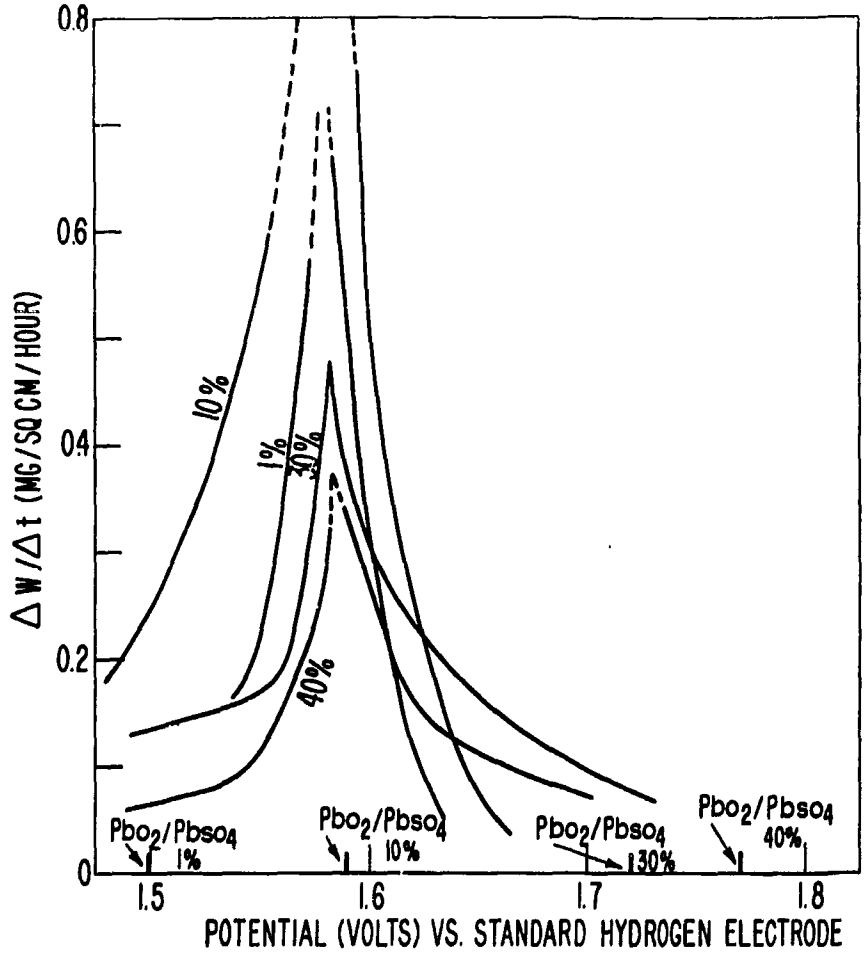

Fig. 22 - Data of Fig. 21 vs. potential referred to the standard hydrogen electrode

change which makes the solid-phase reaction spontaneous to the extent of 38.2 kg cal or, in its voltage equivalent, 0.83 volt. So if this value is substracted from 1.58, the estimated value for the peak of the curve, a value of +0.75 volt results and this value may represent the point of zero charge on the lead metal.

The other conclusion relates to the idea (offered before) that on discharge the solid-phase reaction might go, breaking up the protective PbO_2 film at the metal-oxide interface and introducing an intermediate PbO layer, contributing to the corrosion.[3] It is now evident from Fig. 21 that unless the positive plate is polarized to the extent of 0.15 to 0.25 volt, PbO will not be formed by the solid-phase reaction in cells operating with ordinary acid strengths. This does not occur except on very high rate discharges, or unless the cell is discharged beyond the knee of the curve. Consequently, it is to be expected that for cells in ordinary operation PbO_2 will always be found next to the metal surface, and that the characteristics of this PbO_2 film will be important in determining corrosion rates.

THE CORROSION PROCESS AT DISCHARGE POTENTIALS

The most important characteristic of the PbO_2 film is obvious: on discharge of the cell, it is converted to $PbSO_4$. The $PbSO_4$ formed is comparatively loose and porous, so that the PbO_2 film which had formed an effective barrier to corrosion during the previous charge is broken down and corrosion by the reaction $Pb + 2H_2O \overset{4e}{\rightleftharpoons} PbO_2 + 4H^+$, can proceed apace.

The factors which control the corrosion rates at these potentials can be determined from the data of Figs. 14 through 17 for the 30% acid. If the total weight loss is plotted vs. time on a log-log plot the curves of Fig. 23 are obtained. The slopes of these curves all lie close to 0.6. The data for the formation of divalent product is plotted on a log-log scale in Fig. 24. Since the slopes of these curves are all very close to 0.5, the experimental equation for the formation of $PbSO_4$ is $w = kt^{0.5}$ and the data are accurately parabolic.

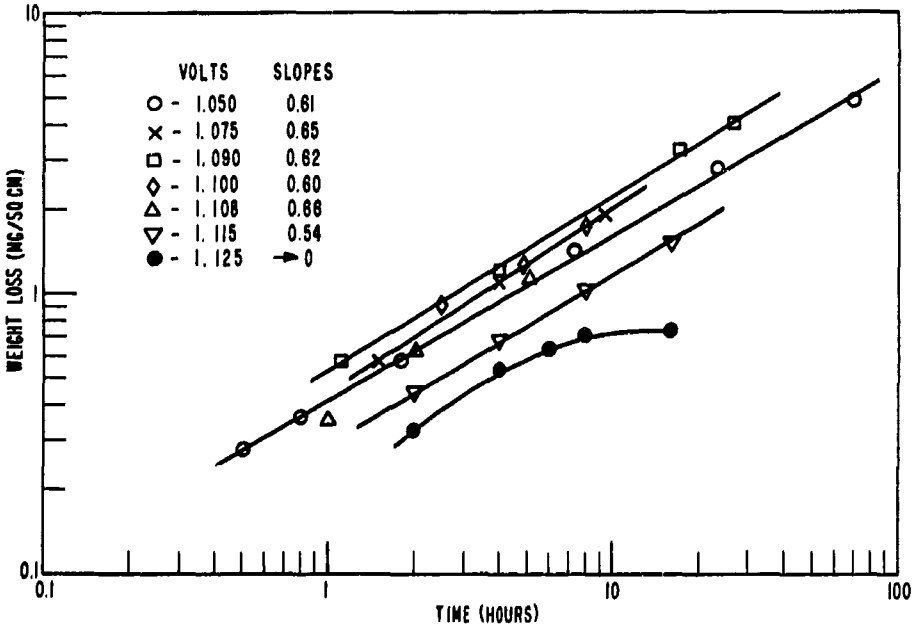

Fig. 23 - Data of Figs. 13-17, log of weight loss vs. log of time

This suggests that the rate of conversion of the PbO_2 film is diffusion controlled (as is the discharge of positive plates)[8] according to Eq. 8. If this is true, and if the other factors of the equation are constant, then the slopes of the w^2 vs. t curves at the various potentials should be proportional to $c_0 - c_1$, the concentration gradient driving the conversion reaction. The w^2 vs. t curves are shown in Fig. 25. Because the reaction is $PbO_2 + SO_4^= + 4H^+ \overset{2e}{\rightleftharpoons} PbSO_4 + 2H_2O$ the rate may be expected to be limited by diffusion of $SO_4^=$ ions. The concentration gradient of $SO_4^=$ ions may be calculated

from the potential and the data[9] of Harned and Hamer, assuming that concentration polarization theory is the same as concentration cell theory in the usual fashion. A plot of the slopes of the w^2 vs. t curves of Fig. 25 against the concentration gradient gives a straight line, as shown in Fig. 26, indicating that the conversion of PbO_2 is actually a diffusion-controlled process.

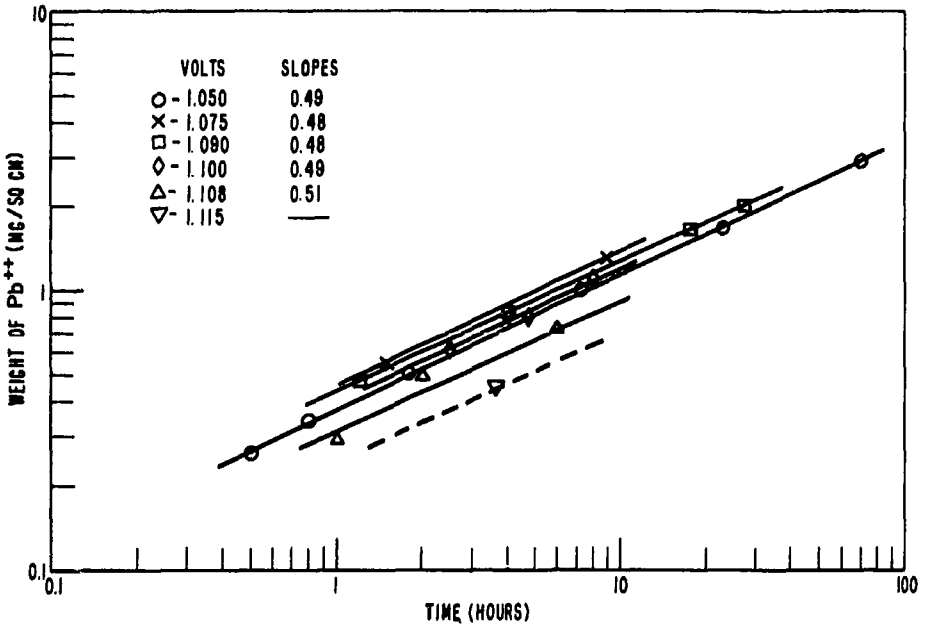

Fig. 24 - Data of Figs. 14-17, log of weight of Pb^{2+} in corrosion film vs. log of time

Thus it is evident that the total corrosion at discharge potentials is the sum of two processes: the oxidation of the metal by the reaction $Pb + 2H_2O \overset{4e}{=} PbO_2 + 4H^+$, and the conversion of the PbO_2 formed by the normal discharge reaction at the positive plate, $PbO_2 + SO_4^= + 4H^+ \overset{2e}{=} PbSO_4 + 2H_2O$. The conversion reaction keeps the PbO_2 film from building up to the thickness at which it becomes protective. At the same time, the total corrosion proceeds somewhat faster than the conversion reaction because the conversion reaction actually undercuts PbO_2 and isolates it electrically (as illustrated in Fig. 27) so that it cannot go to $PbSO_4$. This process allows quantities of PbO_2 much larger than necessary for a protective film to be present in the reaction product, as can be seen by comparing Figs. 14 and 16 with Fig. 11. Nevertheless, the rate is controlled by the conversion reaction, which is itself diffusion controlled. Such a process would explain the slopes of the curves of Fig. 23, which show a value of 0.6 rather than 0.5. Therefore it is not quite the rate of conversion of the PbO_2 film which limits the over-all rate, but more exactly it is the rate of penetration of the conversion process into the underlying film. Mathematically this may be described by the empirical equation

$$w = c_1 t^{1/2} + c_2 t.$$

If the rate of corrosion at constant weight loss is plotted vs. potential, the curve shown in Fig. 28 is obtained. The numbers at the points show the percent of current going to divalent product. Ordinarily, the curve would be expected to follow the course of the dotted line as the concentration gradient approaches the maximum value limited by the concentration in the body of the solution. The reason for the minimum at

1.050 volts is not understood. The rapid rise in the rate below about 1.025 volts is indicative of a new reaction which is, of course, the beginning of the solid-phase reaction. The rate goes up because the underlying PbO_2 film is attacked from the metal side as well as from the solution side, rendering the film more porous.

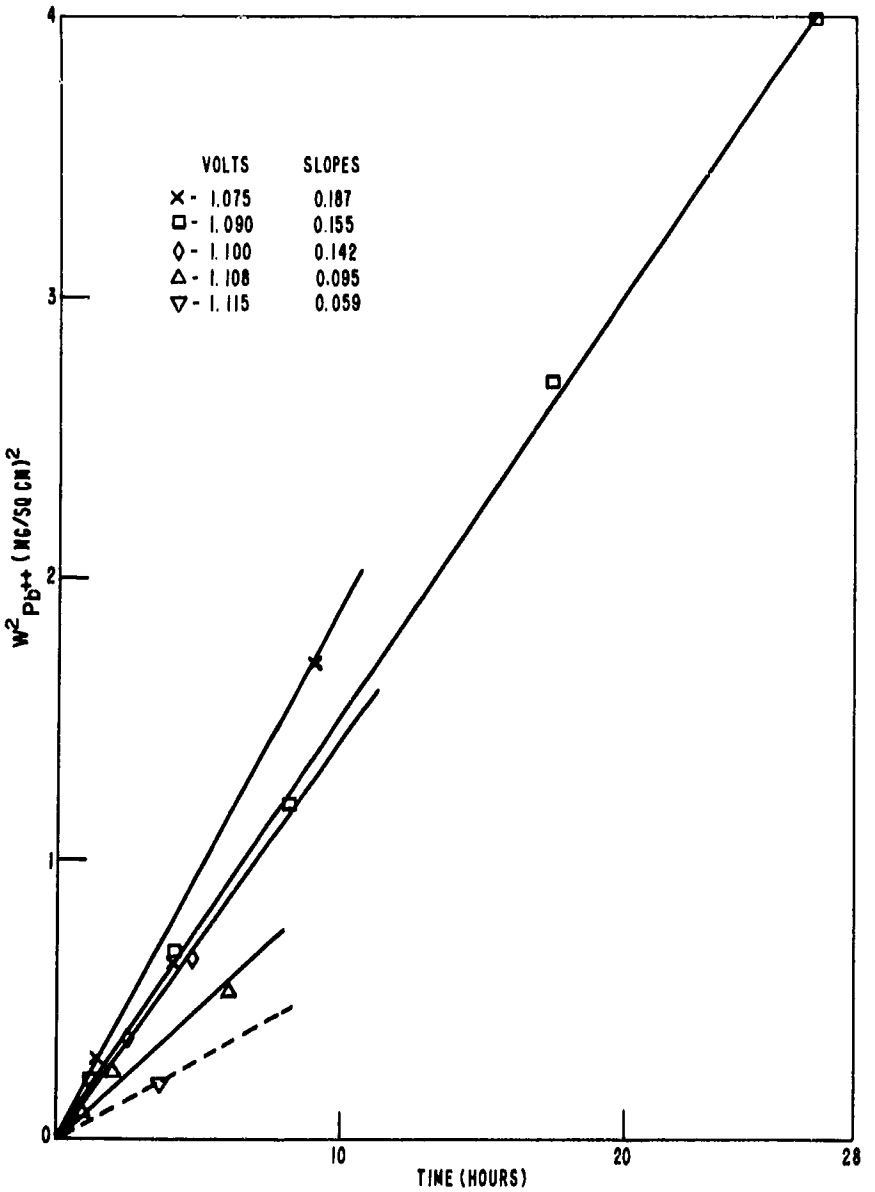

Fig. 25 - Data of Fig. 24, square of weight of Pb^{++} in film vs. time

THE CORROSION PROCESS ABOVE THE REVERSIBLE POSITIVE-PLATE POTENTIAL

It remains to consider corrosion at voltages corresponding to float conditions, i.e., above the reversible $PbO_2/PbSO_4$ potential. It is apparent that the data are insufficient, during the time of rapid film formation, to characterize the mechanism definitely. Table 3 shows the rates, determined from the linear portion of the curves, as a function of potential, acid strength, and temperature. There seems to be a trend toward higher rates at higher temperatures and lower acid concentrations. The effect of potential is uncertain, but must be small, from the data for 30% acid at 30°C.

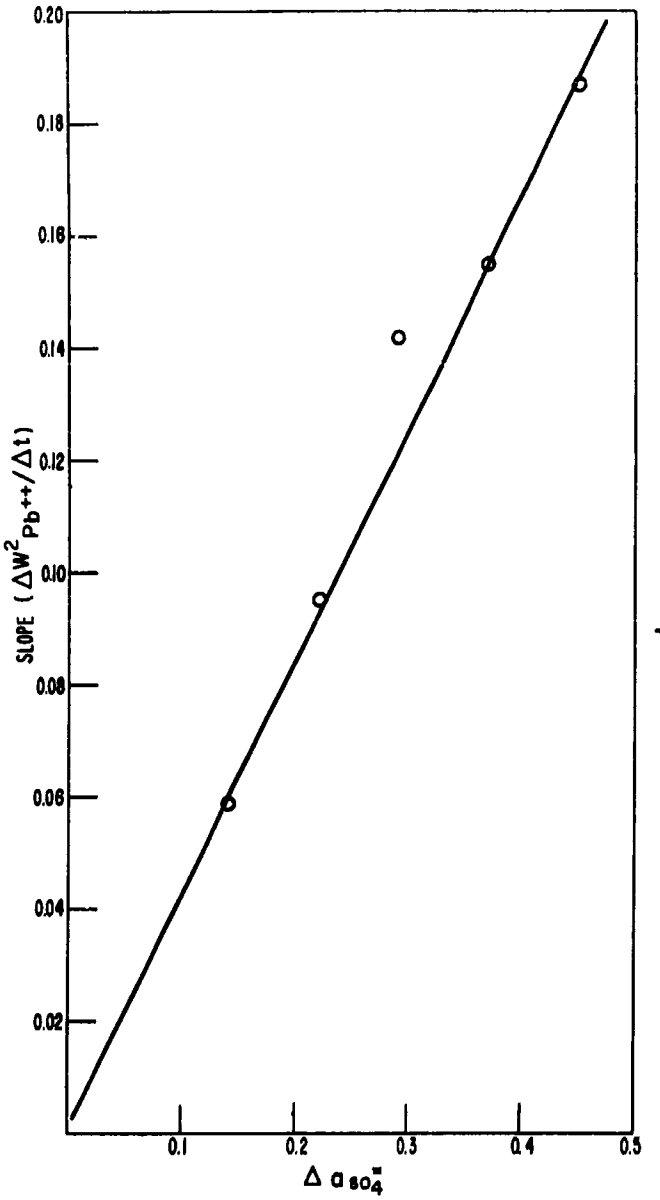

Fig. 26 - Slopes of Fig. 25 vs. $\Delta a_{SO_4^=}$

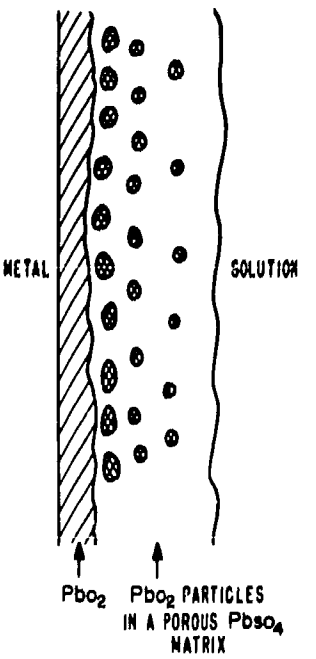

Fig. 27 - Illustration of corrosion film

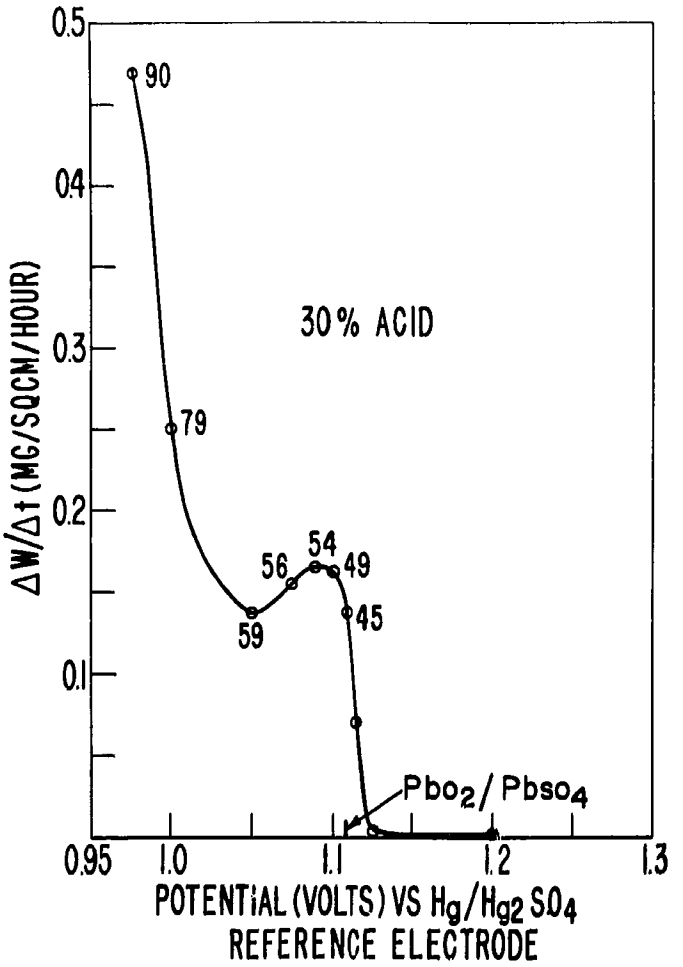

Fig. 28 - Corrosion rate at constant weight loss (1.18 mg/sq cm) just below the $PbO_2/PbSO_4$ potential

In spite of the fact that it is concluded that a definite mechanism cannot be ascertained from the data, a discussion of possibilities may not come amiss. Examination of the data of Figs. 10, 11, and 12 shows that something occurs in the film which slows down the rate rather sharply after the period of rapid film build-up. Theoretically, it has been shown that when corrosion proceeds by migration of ions through solid films, certain types of film breakdown such as blistering can result in a rate lower than that given by the parabolic law which governs the diffusion of ions through solids.[10]

This is readily understandable by considering such breakdown in terms of the parabolic law, which gives the rate of film growth dy/dt as a function of the area a and the length of the diffusion path l

$$\frac{dy}{dt} = \frac{ka}{l}.$$

For a complete film l = y and the parabolic relationship results. If film rupture should occur in the form of blisters which have no channels to the surface to allow ingress of electrolyte, the blisters will offer additional resistance to migration of ions by decreasing a and increasing l, resulting in a much-decreased corrosion rate. In such a case, a complete compact film would actually be undesirable.

TABLE 3
Corrosion Rates Above the $PbO_2/PbSO_4$ Potential

% Acid	Voltage	Penetration Rate (cm/year)	
		30°C	50°C
10	1.15	3.0×10^{-3}	3.5×10^{-3}
	1.20	4.2	4.3
	1.25	3.0	7.7
30*	1.125	1.5	
	1.20	1.2	2.1
	1.25	1.3	2.4
	1.30	0.9	3.9
40	1.25	0.4	1.5
	1.30		2.8
	1.35	0.9	3.3

* Bell Telephone's value for 0.006% Ca grid in 1.210 acid is 1.3×10^{-3} cm/year

The parabolic law assumes a linear, ionic diffusion gradient, which is not necessarily the case. The effect of nonlinearity would be to make the rate fall off faster with thickness than would be indicated by the parabolic law; even assuming a continuous film, so such an explanation may also be possible.

Continuous film or not, however, such an ionic diffusion gradient might possibly be responsible for the oft-observed high voltage of the positive plate at the end of charge. This voltage increment above the reversible potential may take hours or days to drift back to the open-circuit value.

DISCUSSION IN TERMS OF BATTERY SERVICE

Concerning cells on float — corrosion may proceed at very low rates of the order of $1\text{-}3 \times 10^{-3}$ cm penetration per year for pure lead. Although no real attempt has been made to establish a definite mechanism for this process, it appears to offer a minimum value for corrosion of positive grids in service; certainly if cells under other conditions of service could be made to approach this value, the increase in life would be more than satisfactory. If the data of Table 3 are reliable, it is indicated that some life might be gained for batteries on float by changing to stronger acids than are usually used (~30%). It is also indicated that the positive plate may be maintained over a rather wide range of voltage (e.g., 1.125-1.30 for 30% acid at 30°C) without much effect on the corrosion rate, and that rigid voltage control may not be necessary. It is by no means impossible, however, that were these tests extended to considerably longer times, small differences in the values of rates would become apparent. These could be appreciable on their effect on life of a cell, which is measured in terms of years. For example, it can be estimated that a minimum corrosion rate of 1.2×10^{-3} cm per year rather than 1.5×10^{-3} cm per year could result in a life of 16.7 years compared to 13.4, an increase of 12%.

In the past, antimonial alloys were used for grids of cells in float service, as for other types of service. Recently, it has been indicated that a binary alloy of calcium and lead might be more suitable, for several reasons, for this type of service.[11] With the antimonial alloys, float voltages were governed by the necessity for supplying enough

current to the negative plates to keep them in good condition. With the calcium alloy the negative plate is no longer a problem, and at the same float voltages much smaller currents (of the order of one-tenth to one-seventieth) [12] will suffice for the negative plate. There may, however, be danger that, at the lower currents, the positive-plate voltage will be lowered enough to drop below the range where PbO_2 forms in a protective coat. If such were to be the case, higher float voltages than were used for the antimonial cells would be necessary to secure the life-increase expected of this alloy. Long-term tests should be run to determine whether a corrosion rate minimum exists in the protective potential range.

Dropping down on the voltage scale, the next potential range for consideration is one in which a large proportion of the lead-acid batteries made today operate, i.e., the automobile battery, which alternates between a stand condition and float, with short high-rate charge and discharge periods. The times on charge and discharge are relatively short and may probably be neglected in considering life.

It appears from Fig. 28 that the life of the positive grids of automobile batteries should approach that of the same batteries on float, the life being shortened somewhat by the time it spends on stand, during which time it will be located somewhere on the steep portion of the corrosion curve at the reversible $PbO_2/PbSO_4$ potential. If most of the stand time were spent at the bottom of this steep curve, then the reduction in life should be small — a likely condition for batteries of cars that are run daily, because it takes an appreciable time for the positive-plate voltage to fall to the open-circuit value after a charge.

A peculiarity of automobile-battery service may be expected to become important as the end of life approaches, i.e., the constant-voltage charge. As the cell gets older, the hydrogen overvoltage at the negative plate falls off for batteries with antimonial grids, which means that the voltage at the positive plate increases proportionately; when this voltage gets in the gassing range, rapid corrosion during the time the car is running will ensue, hastening the end of life. Furthermore the time spent at these higher positive-plate voltages will be longer during the time the car is running, with the same effect.

Batteries which operate under a cycling program, such as industrial truck and submarine batteries, spend an appreciable part of their life on discharge, and during the discharge they will be well up on the steep portion of the corrosion-rate curve previously mentioned. This is unquestionably the reason why batteries in cycling service have relatively short lives in comparison with batteries in other types of service. This effect of the time-on-discharge has also been observed in a laboratory study designed to show such an effect. [13] It was observed that the total amount of corrosion doubled as the percent of discharge time increased from 15 to 75. Of more practical importance, however, it more than doubled as the percent of discharge time increased from zero to 15.

As mentioned before, batteries with electrolyte strengths ordinarily used will not spend any appreciable amount of time in the voltage range where the solid-phase reaction can occur; corrosion during discharge will be limited by the rate of diffusion of $SO_4^=$ into the corrosion film, and only PbO_2 and $PbSO_4$ should be found in the corrosion product, with PbO_2 being next to the metal. It is also expected that, as the film builds up in thickness, the rate at which $SO_4^=$ can diffuse to the corroding surface will slow down until eventually it becomes less than the linear rate observed for stand conditions. Then the rate should become the same as that for the linear rate on stand, which does not depend on film thickness. This has been observed. [14]

The theory presents two obvious methods of attack on the problem; the diffusion coefficient can be made smaller by increasing the viscosity, and possibly the diffusion path could be made tortuous or the pore area smaller. Attempting to lower the diffusion coefficient will boomerang, because it will lower the rates and energies which can be drawn from the cell, inasmuch as the active material discharge depends on this factor.

The viscosity of the electrolyte could be increased considerably by increasing the acid strength, and lower initial corrosion rates are actually found.[3,14] However, such an expedient can be utilized to a limited extent only, before the negative plate begins to show decreased capacity.[15] In addition, although initial corrosion rates are higher in low-gravity acids, they slow down much faster, and after a time the corrosion rate in the high-gravity acids becomes larger.[13,14] On the whole, it is concluded that not much may be gained in this way. Methods of affecting the pore area and path length are not immediately evident; furthermore, it is possible that they depend primarily on acid strength. Apparently, what must be done is to find some method or trick of selectively preventing the normal discharge reaction from taking place at the PbO_2 coating on the grid.

SUMMARY

Anodic corrosion of lead in sulfuric acid was studied over a wide potential range using constant-potential techniques. In general, it was found that the elctrochemical reactions expected on the basis of the thermodynamic data occur at their proper potentials. There are several of these reactions, and in addition certain chemical reactions also occur. The whole picture is rather complicated, and rates of corrosion are found to be controlled by different reactions and factors in different potential ranges.

Mechanisms which limit corrosion rates have been determined for two of the potential ranges. In other areas, qualitative descriptions of the rate curves are possible, but additional work must be done to establish the rate-controlling factors satisfactorily.

Data for the several ranges may be interpreted, more specifically, to show the following:

1. PbO_2 begins to be formed on lead at its reversible potential (E_0 = +0.666) calculated from the reaction $Pb + 2H_2O \rightleftharpoons PbO_2 + 4H^+ + 4e$. It is unstable, and does not show up in the reaction product until considerably higher voltages are reached, for three reasons: (a) it may react at the Pb/PbO_2 interface to form PbO by the solid phase reaction $PbO_2 + Pb \rightleftharpoons 2\,PbO$; (b) it may react with H^+ below the reversible potential (E_0 = +1.100) for the reaction $PbO + H_2O \rightleftharpoons PbO_2 + 2H^+ + 2e$; and, (c) it may react with H^+ and $SO_4^=$ below the reversible potential (E_0 = +1.684) for the normal reaction occurring at the positive plate of the lead-acid cell $PbSO_4 + 2H_2O \rightleftharpoons PbO_2 + H_2SO_4 + 2H^+ + 2e$.

2. A voltage limit above which the solid-phase reaction cannot go has been established to be about +1.58 volts with reference to the standard hydrogen electrode. This voltage marks the appearance of PbO_2 in the reaction product and is characterized by a peak in the corrosion-rate vs. potential curve which separates the kinetic behavior of the corrosion processes. At potentials less noble than that of the peak, rates of corrosion are limited by the resistance of the electrolyte in a porous PbO film and of course, by the driving potential. At potentials more noble, just below the reversible positive-plate potential, corrosion-rates are limited by rates penetration of the positive-plate discharge reaction into an underlying PbO_2 film. This penetration is controlled by diffusion of $SO_4^=$ toward the PbO_2-solution interface through a porous film of mixed PbO_2 and $PbSO_4$. At slightly less-noble potentials, diffusion control gives way to a relatively rapid process because the solid-phase reaction begins to take place, the underlying PbO_2 film is attacked from both sides, rendering it more porous.

3. Above the reversible, positive-plate potential, corrosion rates fall off very rapidly to extremely low values, apparently constant with time, because PbO_2 is the sole product, and it can build up to thicknesses which make it protective. These low rates are not voltage-sensitive within experimental error, but they do seem to increase with increasing temperature and decreasing acid concentration.

Gains in knowledge of the corrosion problem resulting from this work do not appear to indicate definite means of slowing down the corrosion rates in cycling cells by tampering with the factors which control the natural processes. This conclusion is arrived at by considering the conflicts which arise out of the over-all cell operation. For example, to slow down appreciably the corrosion process in cycling cells, it would be necessary to slow down the diffusion-controlled penetration of $SO_4^=$ ion into the PbO_2-$PbSO_4$ film on the grid. Yet, the electrical capacity of the positive plate is limited, except at low rates, by diffusion of the electrolyte and hence everything is done to facilitate diffusion. Other aspects of cell life are also considered in terms of these results.

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